1 Introduction

On November 5, 1998, the Air Resources Board considered regulations that set emission standards for Low Emission Vehicles (LEV-II). Included in the regulations were tighter standards for emissions of nitrogen oxides (NO_X). During the LEV-II hearing, several witnesses suggested that lower NO_X emissions would be counter-productive for reducing ozone concentrations. As justification, these witnesses cited a phenomenon known as the “ozone weekend effect.”

The “ozone weekend effect “ refers to the interesting observation that ozone measurements in some locations are typically higher on weekends compared to weekdays. Examples of the ozone weekend effect can be seen in **Error! Reference source not found.**. The effect occurs when the solid line is above the dotted line in each graph.

The ozone weekend effect is somewhat surprising because smog-forming emissions mostly come from sources, such as cars, trucks, and factories, that could be expected to produce a lower total of smog-forming emissions on weekends compared to weekdays.

After evaluating all of the testimony at the LEV-II hearing, the Board adopted the proposed regulations and directed the CARB staff to investigate the ozone weekend effect. The purpose of the study was to determine why the ozone weekend effect occurs and whether it demonstrates that NO_X reductions in California are counter-productive for reducing ozone.

In response to the Board's directive, the staff identified analyses using presently available data to investigate the ozone weekend effect. The analyses focused primarily on the South Coast Air Basin of California because of its rich stores of data from routine monitoring and special field studies. This report summarizes the results of the staff’s work and recommends further research to address unresolved issues.

Objectives of this report

Previous studies of the ozone weekend effect have established that the ozone weekend effect is real but have not determined its cause(s). Some investigators have speculated concerning the cause(s) of the ozone weekend effect, but definitive answers were beyond the scope of their work.

The objectives of this report are to examine the ozone weekend effect, determine its magnitude, identify its causes, and evaluate its implications concerning ozone control strategies. These objectives are challenging; data may be sufficient for some but insufficient for others. In addition, the implications may not be straightforward because the context and the results of intermittent <u>weekend</u> emission reductions may be quite different from the context and results of consistent <u>regulatory</u> emission reductions.

Background

Ozone formation

Very little ozone is directly emitted by pollution sources. Rather, it is formed in the atmosphere through a complex set of chemical reactions initiated by ultra-violet sunlight. The chemical reactions chiefly involve volatile organic compounds (VOCs) and NO_X ($NO + NO_2$).

Without VOCs and NO_X from human activities, ozone concentrations near the surface of the earth would be limited to approximately 20 to 40 parts per billion (ppb). When anthropogenic VOCs and NO_X are present, however, ozone concentrations can reach levels that compromise human health. Federal and state standards for ozone indicate that concentrations from 85 to 120 ppb for one hour or more can adversely affect lung function.

Ambient ozone (O_3) is formed from the reaction of free oxygen atoms with molecular oxygen (O_2). The main source of free oxygen atoms in the lower atmosphere (troposphere) is photolysis of nitrogen dioxide (NO_2), a constituent of NO_X. During photolysis, NO_2 absorbs ultra-violet sunlight and dissociates into NO and a free oxygen which rapidly combines with O_2 to form O_3. Ultra-violet solar radiation, NO_2, and VOCs are needed to drive the complex ozone-forming processes.

The importance of NO_2 photolysis is illustrated by an interesting observation. When VOCs are weighted by their ozone-forming potential (reactivity), ozone concentrations in very different environments are strongly correlated with NO_X concentrations but only slightly correlated with VOC concentrations (Seinfeld & Pandis, 1998).

The relationship between ozone, NO_X, and VOCs is complex. For example, NO_X promotes ozone formation when VOCs are relatively abundant but restricts ozone formation when VOCs are relatively scarce. More specifically, when the VOC/NO_X ratio is greater than 8 to 10, NO_X tends to promote ozone formation, but when the VOC/NO_X ratio is less than 8 to 10, NO_X tends to restrict ozone formation. The VOC/NO_X ratio, in turn, can differ by location and time-of-day within a geographic area (Seinfeld and Pandis, 1998; Finlayson-Pitts and Pitts, 2000).

The effect of the VOC/NO_X ratio may not be constant, however. Experiments in the 1990s indicate that the "reactivity" of VOCs decreases as NO_X decreases. Therefore, an increase in the VOC/NO_X ratio when emissions are high may lead to a greater proportional increase in ozone compared to the same increase in the VOC/NO_X ratio when emissions are lower (Carter, 1995).

The ozone weekend effect

The ozone weekend effect is not new. For the last 30 to 40 years, atmospheric scientists have noted that ozone concentrations can be somewhat higher on weekends than on weekdays at some locations (Levitt and Chock, 1976; Elkus and Wilson, 1977). This is interesting because concentrations of ozone precursors seem to decrease on weekends almost everywhere. Atmospheric scientists coined the term "weekend effect" to describe the phenomenon.

Before the 1990s, analyses of the ozone by day of week effect seldom found statistically significant differences, although patterns were consistent from study to study. Quantitative estimates of the differences were highly uncertain. In the 1990s, however, studies used additional data and improved analytical methods to show the ozone weekend effect is “real.” One recent study provided quantitative estimates of the ozone weekend effect in three regions of California – the South Coast Air Basin, the San Francisco Bay Area Air Basin, and the Sacramento Metropolitan Area (Austin and Tran).

A large body of weekday-weekend studies has revealed the following facts about the ozone weekend effect:

- It occurs in many parts of the world
- It is most commonly associated with urban rather than rural locations
- It can be seasonally dependent
- It can change over time (e.g., from Saturday to Sunday)
- It may persist despite downward trends in ozone on all days of the week
- No other major pollutant behaves like ozone

Ozone control strategies in California

The Air Resources Board is charged with protecting the public health and welfare from the adverse effects of pollution. To reduce health risks due to ozone and some other pollutants, the ARB has followed a policy for more than 20 years of reducing emissions of both VOCs and NO_X.

From the mid-1970’s into the 21st century, the ozone control strategy implemented in the SoCAB included reductions of both VOC emissions and NO_X emissions. Early NO_X reductions were achieved by statewide controls on emissions from motor vehicles combined with local controls on emissions from industrial sources, such as cement kilns.

Additional benefits of this policy include reductions in nitrogen dioxide, particulate nitrates, acid deposition, and certain toxic air contaminants.

The policy of reducing VOCs and NO_X concurrently has been pursued most vigorously in the South Coast Air Basin, where it has been dramatically successful. As seen in Figure 1-1, the frequencies of unhealthful ozone concentrations have declined steadily in the past 35 years. In 1970, Stage II episodes (350 ppb or more) occurred on 70 days per year but were completely eliminated by 1989. Stage I episodes (200 ppb or more) occurred on 180 days per year but are now quite rare. Even exceedances of California’s protective state standard (90 ppb) have been reduced more than 60 percent.

Other measures of ozone air quality confirm the record of success for combined reductions of VOCs and NO_X. Figure 1-2 tracks the changes in “peak” ozone concentrations for the past 35 years. Peak concentrations have been reduced approximately 70 percent during this period. Though more remains to be done to achieve national and state standards, the success of concurrent VOC and NO_X reductions is very impressive.

Ambient air quality status and trends

During the late 1960s and much of the 1970s, the highest ozone concentrations (Stage II and Stage III episodes) in the SoCAB occurred most frequently on Thursdays and Fridays with Sunday having the fewest episodes (Figure 1-3 and *CARB, 1978*). A Stage II episode occurs when a 1-hour ozone concentration is 350 ppb or more. A Stage III episode occurs when a 1-hour ozone concentration is 500 ppb or more. It is interesting to note that none of the 14 Stage III episodes between 1964 and 1977 occurred on a weekend (Figure 1-3). Nevertheless, some sites, primarily in the western portion of the basin where ozone concentrations are relatively low, typically had higher ozone concentrations on Sundays than on weekdays.

While ozone concentrations declined generally in the SoCAB, the rate of improvement on weekends was somewhat slower than the rate of improvement on weekdays. Over the years, typical weekday concentrations of ozone became smaller than typical weekend concentrations. By the late 1990s, Sunday became the day with the most ozone episodes instead of the fewest. The term "ozone weekend effect" was coined to describe this tendency for ozone concentrations to be greater on weekends than on weekdays. This phenomenon coincides with presumably lower emissions of VOCs and NO_X on weekends compared to weekdays. Ambient data indicate that the concentrations of carbon monoxide (CO) and NO_X on weekends decline proportionally more than VOCs.

Between 1987 and 1997, ozone concentrations declined for all days of the week at all locations in the SoCAB. Less progress has occurred in the San Francisco Bay Area, the Sacramento Valley, and the San Joaquin Valley. VOC control plans are in place in these air basins. However, the SoCAB NO_X control plan is significantly more aggressive than the others which rely heavily on statewide controls on motor vehicles. From 1987 to 1997, peak ozone concentrations declined on average by 33 percent in the SoCAB but only 9 percent in the SFBAAB, 10 percent in the Sacramento Valley, and 5 percent in the San Joaquin Valley. Although the SoCAB may also have the most aggressive VOC controls, the NO_X reductions may also be an important factor in improved ozone air quality in the SoCAB.

Analytical strategies, findings, and issues

Data from areas with different meteorology, a different mix of emission sources, and different control programs may help elucidate the ozone weekend effect. For example, in clean environments, unaffected by anthropogenic emissions, one would expect no difference between ozone concentrations on weekdays and weekends. In NO_X-limited areas, one might expect the lower NO_X on weekends to result in lower ozone concentrations on weekends. In VOC-limited areas, one might expect the lower NO_X on weekends to result in higher ozone concentrations on weekends.

However, the behavior of ozone in air basins may differ significantly from the behavior of ozone in most smog chamber experiments or air quality models. In an air basin, initial conditions, boundary conditions, wind fields, clouds, mixing heights, carryover, and hourly input of fresh emissions may all differ significantly from day to day. Such differences are very difficult to simulate using smog chambers. Although photochemical simulation models include these and other details, they do so imperfectly and with uncertain errors and sensitivities. Furthermore, it may not be feasible to validate these models for suitable sequences of weekday and weekend conditions.

Assuming meteorology is unaffected by the day of the week, the fact that patterns of human activity are different on different days of the week is the only reasonable explanation for the ozone weekend effect. Anthropogenic pollutants are emitted at different times and locations on different days of the week. These emissions interact with meteorology (e.g., dispersion, dilution, and deposition) to generate ozone and particulate matter through a complex set of photochemical reactions. To identify the cause(s) of the ozone weekend effect, the temporal and spatial patterns of emission activity, the overall emission inventory, meteorology, and photochemistry will need to be woven together.

Six hypothetical causes of the ozone weekend effect are identified in Chapter 3 of this report. The hypotheses, which are not mutually exclusive, are the following:

- NO_X reductions
- NO_X timing
- Carryover near ground-level
- Carryover aloft
- Increased weekend emissions
- Decreased absorption of UV sunlight

The results of various analyses of ambient air quality and activity data are used to characterize day-of-week patterns and to evaluate for consistency with the hypotheses. Each of these hypotheses includes multiple disciplines that need to be integrated and corroborated in the process of isolating the factors contributing to the ozone weekend effect.

The long-term and extensive monitoring network of the SoCAB, its relatively high pollutant concentrations, and its large population make this area most useful for analyzing the ozone weekend effect. Most of the analyses in this report focus on the South Coast Air Basin. Figure 1-5 shows the locations of air basins in California and highlights the SoCAB. A map displaying topographic features and county boundaries of the SoCAB is provided in Figure 1-6. A map portraying the transportation network of freeways and highways in the SoCAB as well as the core set of monitoring sites that will be referred to in many chapters is presented in Figure 1-7.

This report does not attempt to determine how emissions differ between weekdays and weekends, because currently available data are too limited. Nevertheless, Table 1-1 is provided to indicate the relative strength of major types of emission sources in the SoCAB. Note that mobile sources dominate the emissions of VOCs (labeled ROG in the table), NO_X, and CO. Also note that the contribution of heavy-duty trucks is very significant for NO_X but much less so for VOCs and CO.

In 1972, some coastal sites in southern California – Lennox, Long Beach, and Whittier – had higher ozone concentrations on weekend days compared to weekdays, although emission inventories were believed to be lower on weekends. At other sites in southern California, ozone did not distinguish between weekdays and weekends. Between 1972-73, early in the morning, all southern California sites had higher ozone concentrations on weekend days than on weekdays, *(Levitt and Chock, 1976*).

California's emission control program, then unique in the nation, advocated control of both VOCs (actually, non-methane hydrocarbons, NMHC, a close cousin) and nitrogen oxides (NO_X) emissions. From weekdays to weekends, ambient NO_X concentrations (and presumably emissions) decline proportionally more than NMHC concentrations decline. The ozone weekend effect has since been hypothesized as a side effect of controlling NO_X emissions. Nevertheless, ARB's strategy of concurrent reductions of VOCs and NO_X has substantially lowered ozone concentrations since the 1972-73 levels.

Geographic and temporal outlines of the southern California "ozone weekend effect" have changed over time. In the mid-1980s, ozone concentrations in coastal areas were highest on Saturdays and Sundays, while ozone concentrations in inland areas were highest on Saturdays (*Zeldin and Horie, 1989*). Later, the geographic extent of the ozone weekend effect grew and ozone concentrations on Sundays became the highest of the week, in the downwind areas of southern California. The emission control program remained steady, reducing hydrocarbons and NO_X emissions simultaneously. By any measure, the control program has substantially lowered ozone concentrations since the 1984 to 1986 levels.

Investigators from the University of California, Los Angeles, conducted two studies of the ozone weekend effect in the South Coast Air Basin with particular emphasis on control strategy implications. The first UCLA study considered data collected from 1986 to 1993 (*Blier and Winer, 1996*). The highest ozone concentrations in a week occurred most often from Thursday through Saturday and less often from Sunday through Wednesday.

The study examined ozone concentrations in several sub-regions of the basin, leading to the following findings.

- On a daily basis, maximum ozone concentrations in each sub-region related more strongly to morning NO_X concentrations locally than to NO_X concentrations in any other sub-region. This was true of “downwind” or “receptor” sub-regions as well as “upwind” or “source” sub-regions.
- Surface carryover of NO_X was not an important factor affecting day-of-the-week differences in ozone.
- Daily ozone concentrations, characterized by the average of the highest 10 daily maxima each year, showed the greatest decrease in the areas with the greatest percentage decrease in early morning NO_X concentrations.

Trend analyses indicated that, regardless of the meteorological conditions, generally lower peak ozone values were observed in the latter four years (1990-1993) than in the first four years (1986-1989). By various measures, the control program lowering VOCs and NO_X concurrently had substantially lowered ozone concentrations since the 1990-93 levels.

The second UCLA study analyzed data from 1986 to 1996 and expanded the analysis to include aerosols and particulate matter data (*Blier and Winer, 1999*). Carryover of NO_X was of greater significance from Friday evening to Saturday than at other times of the week. In general however, ground-level observations suggested a small carryover effect at the surface for NO_X and NO_2.

The UCLA studies concluded that the observed day-of-week effects did not necessarily demonstrate that further NO_X control would be counterproductive to further ozone reductions. On Saturdays and Sundays from 1994 through 1995, ambient concentrations were higher for NMHC and NO_X and lower for ozone. However, 1986-96 ozone concentrations declined significantly coincident with significant reductions in levels of NMHC and NO_X. A small day-of-the-week influence was noted for aerosol concentrations and ambient temperatures, indicating some impact attributable to human activities. Additionally and significantly, the study observed a shift to later and shorter ozone seasons, with Sunday becoming the day with the highest ozone concentrations. Again, the ozone control program of concurrent VOC and NO_X reductions substantially lowered ozone concentrations from the 1986 levels.

The data clearly show that the geographic and temporal patterns of day-of-the-week effects on ozone in southern California have changed during the last 30 years. The emission control program simultaneously reduced both VOC and NO_X emissions during this period, and by almost any measure, the dual control program has substantially reduced ozone concentrations. Furthermore, VOC control efforts through fuel reformulation have included substantial reductions of toxic air contaminants such as the human carcinogen, benzene.

References

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Zeldin, M., Y. Horie, and V. Mirabella (1989) “An analysis of weekend/weekday differences in the South Coast Air Basin of California,” Paper 89-125.6, Air & Waste Management Association 82nd Annual Meeting & Exhibition, June 25-30, 1989, Anaheim, CA.

Table 1-1. Annual average emissions of ROG, NO_X, and CO (tons/day) by source category in the South Coast Air Basin, 1995 and 2000

	ROG		NO_X		CO	
Source Category	**1995**	**2000**	**1995**	**2000**	**1995**	**2000**
Stationary Sources	**275**	**279**	**144**	**118**	**71**	**66**
Area-Wide Sources	**228**	**200**	**31**	**34**	**716**	**633**
Mobile Sources:	**826**	**566**	**1007**	**759**	**8435**	**5805**
Heavy-Duty Trucks	61	35	226	348	902	491
Other Vehicles	765	531	781	411	7533	5314
Other Mobile Sources	**108**	**108**	**270**	**268**	**870**	**808**
Natural Sources	**125**	**125**	**Neg.**	**Neg.**	**106**	**106**
Total	**1,562**	**1,278**	**1,452**	**1,179**	**11,416**	**8,138**
Percent Change		**- 18%**		**- 19%**		**- 27%**

NOTES:
Figures for stationary sources and area sources are derived from the California Emission Forecasting System (CEFS) 1996 Base Year Forecast Scenarios for the ARB 2000 Almanac.
Figures for Mobile Sources are from EMFAC 2000 (10/06/2000), where heavy-duty trucks include all trucks weighing 8500 pounds and up.
Figures for Natural Sources are from the following: ROG (Benjamin, et al., 1997, *Atmospheric Environment*, Vol. 31, pp 3087 - 3100); NO_X (negligible natural sources); CO (CEFS 1996 Base Year Forecast Scenarios for 2000 Almanac). No changes are expected in emission rates for natural sources between 1995 and 2000.

Figure 1-1. Number of days per year when the California Ambient Air Quality Standard for ozone was exceeded and when Stage I and Stage II ozone episodes occurred within the South Coast Air Basin, 1965 - 1999

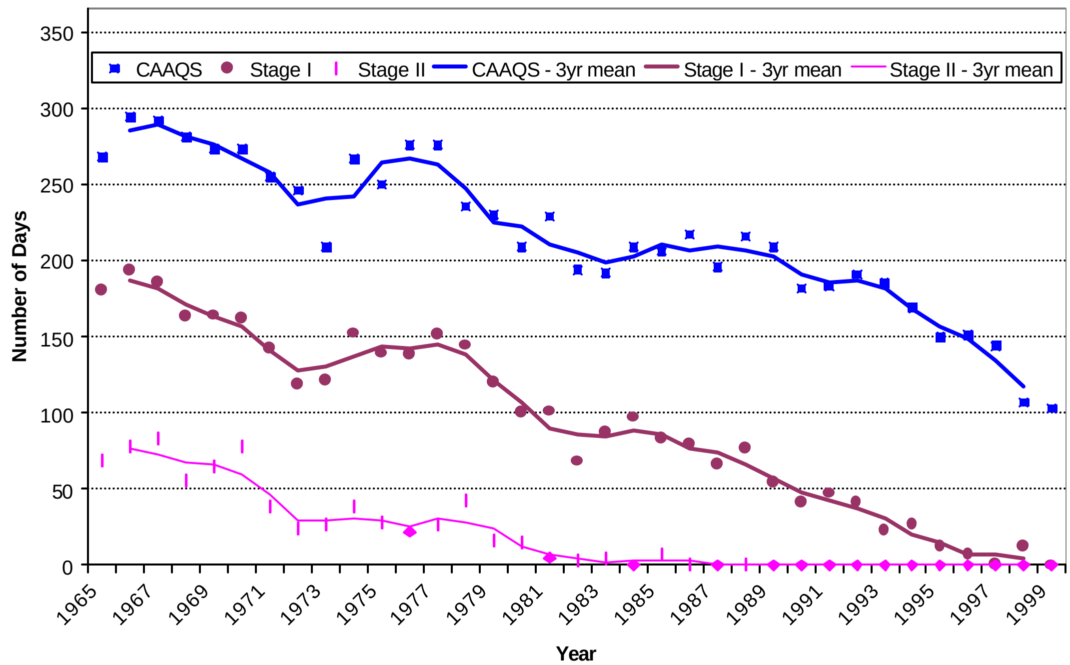


Figure 1-2. Trends of peak ozone concentrations (annual maximum 1-hour and mean of top 30 daily maximum 1-hour) observed in the South Coast Air Basin, 1965 - 1999

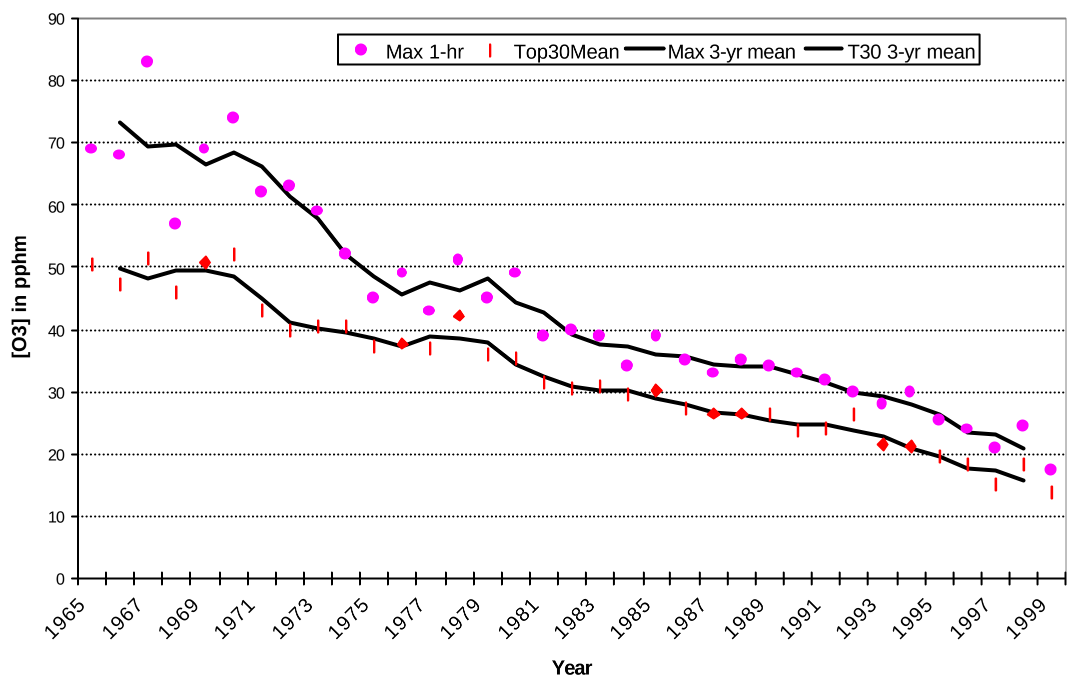


Figure 1-3. Frequency of Stage II and Stage III ozone episodes by day of the week in the South Coast Air Basin, 1964 - 1977.

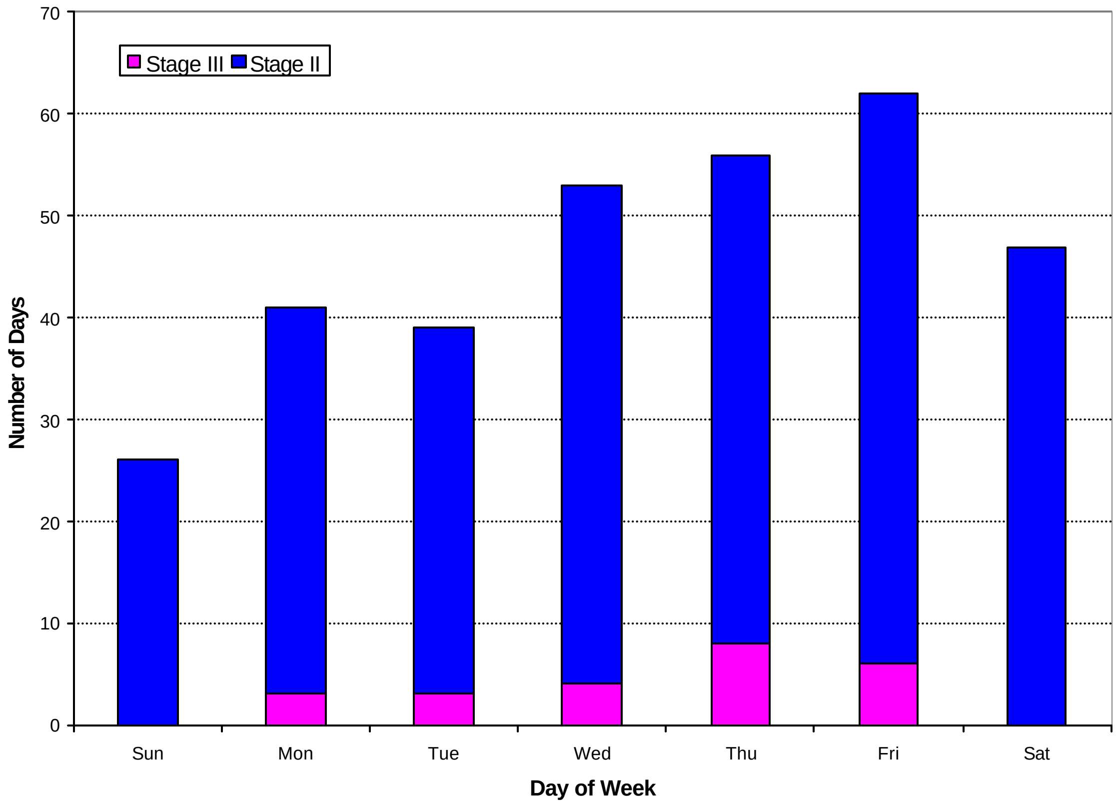
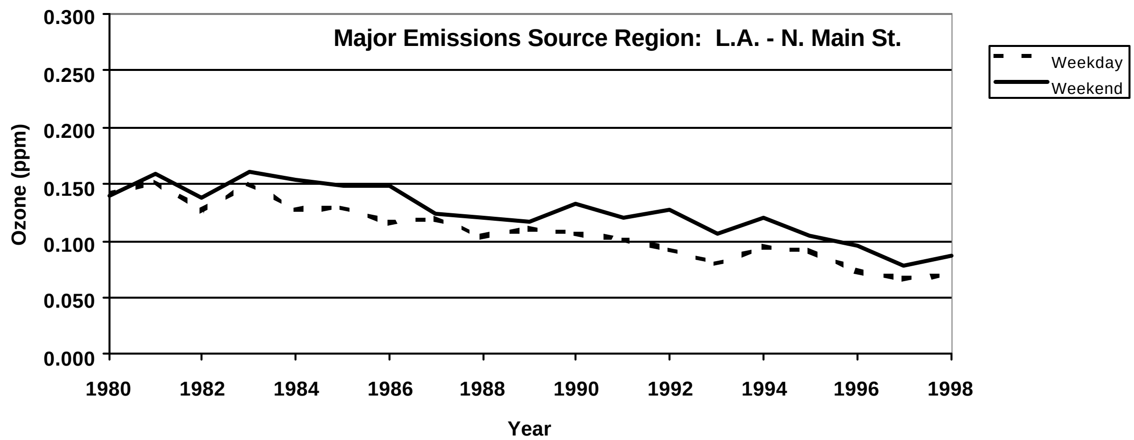
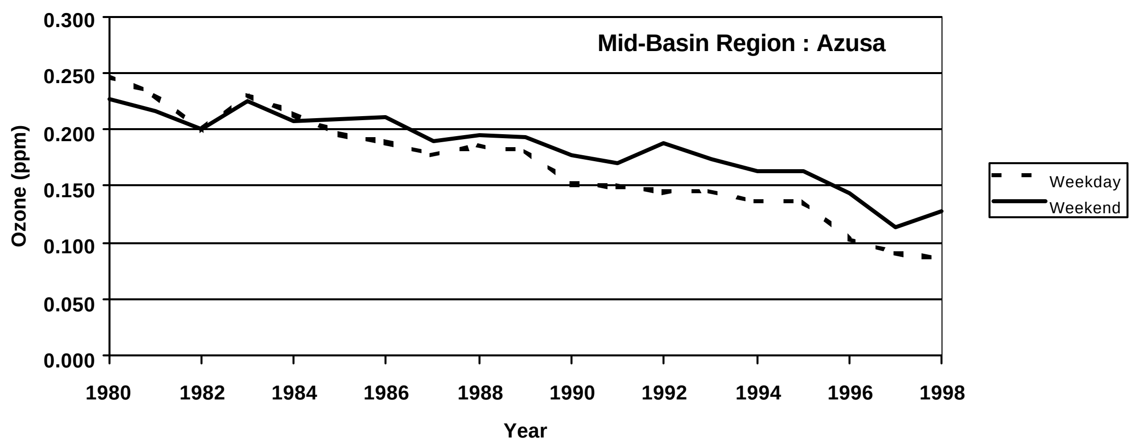


Figure 1-4. Ozone trends from 1980 through 1998 for weekdays and weekends at Azusa, L.A. - North Main St., and Riverside in the South Coast Air Basin.

(Ozone is the mean of the 2nd - 11th highest daily maximum ozone concentrations each year.)





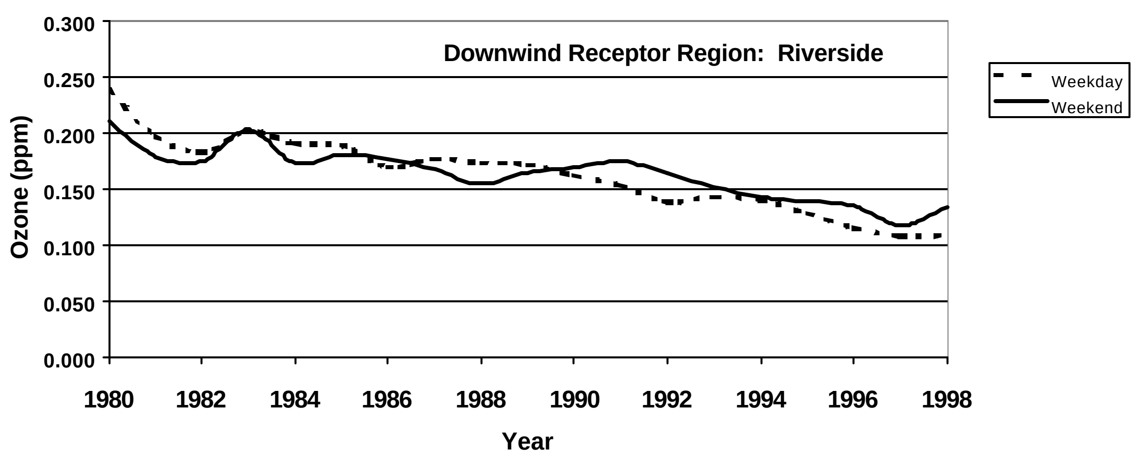


Figure 1-5. Outline of the State of California showing the boundaries of air basins. The South Coast Air Basin, the focus of most analyses in this report, is highlighted to show its location and size relative to the other 14 air basins in California.

Figure 1-6. Map showing the topographic features, counties, and major regions in and around the South Coast Air Basin.

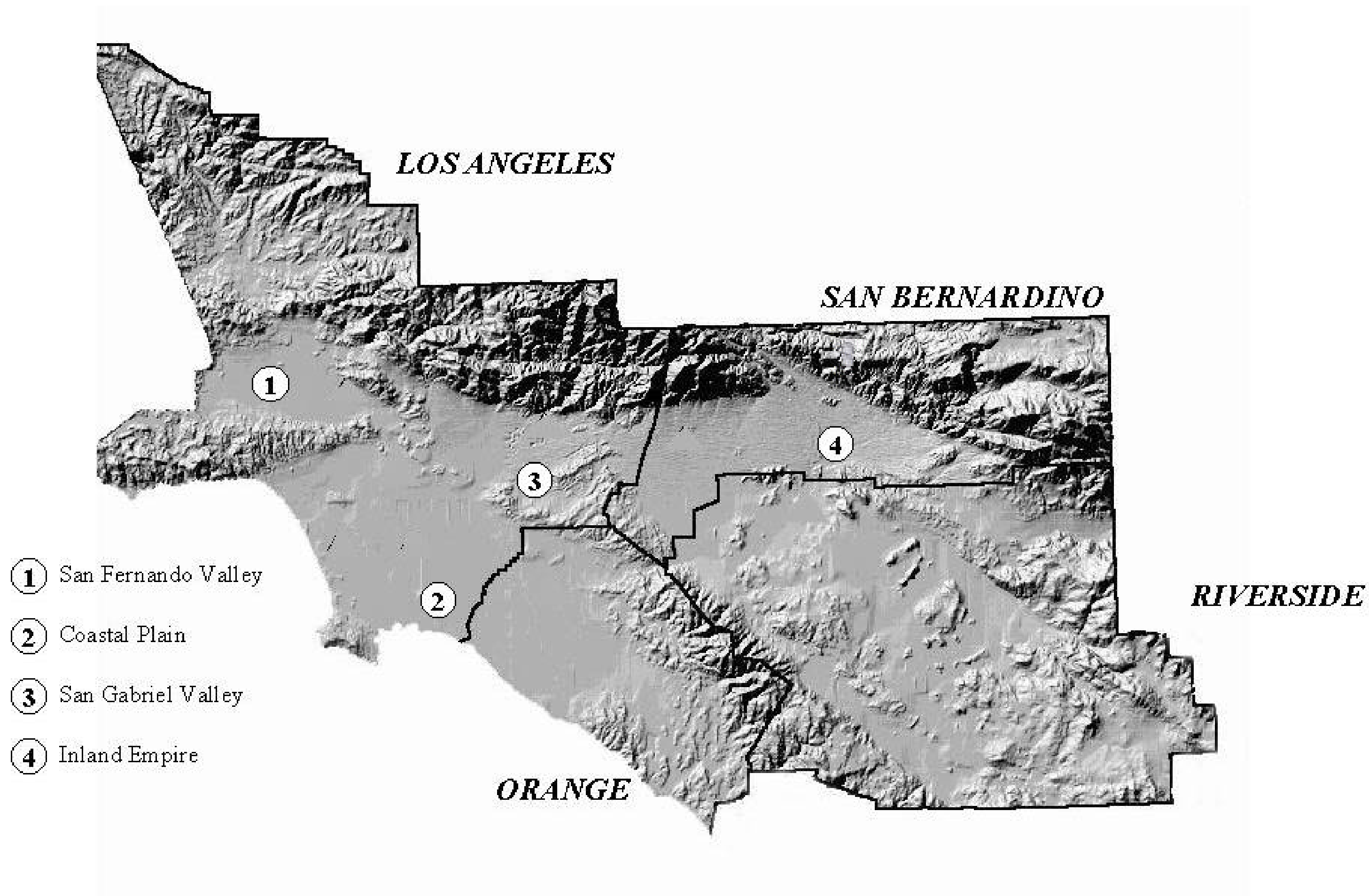
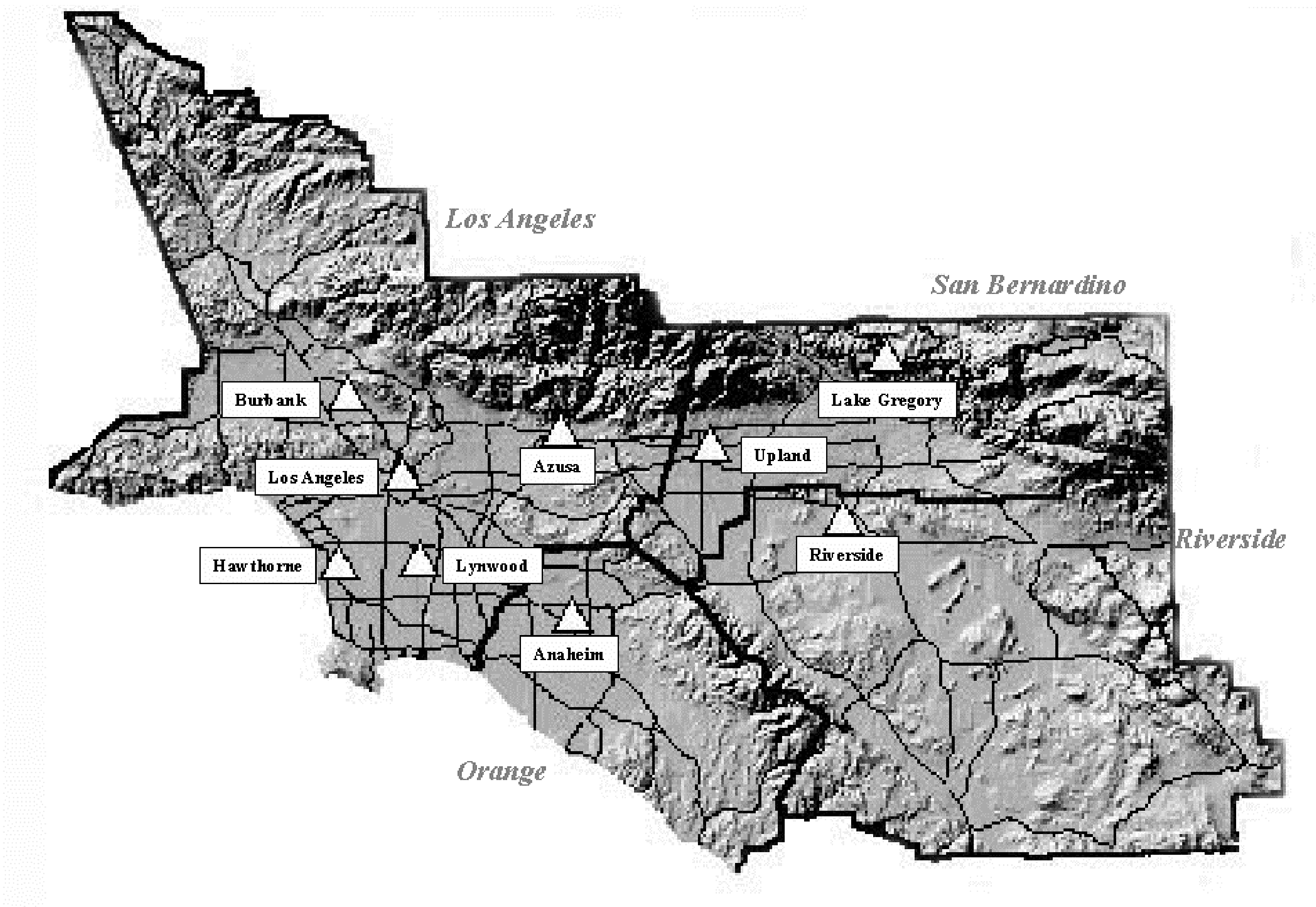


Figure 1-7. Map showing the major freeways and highways in the South Coast Air Basin as well as the locations of the "core" monitoring sites used in many of the analyses in this report.



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